

PERFORMANCE CHARACTERISTICS OF LITHIUM ION POLYMERIC ELECTROLYTE CELLS

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Abstract

A series of polyacrylonitrile-based (PAN) electrolytes containing LiAsF_6 and a number of solvent mixtures including Ethylene Carbonate (EC) + Propylene Carbonate (PC) were prepared, electrochemically evaluated and used as electrolyte in the polymer cells. The typical composition of the electrolyte mixture was PAN ~15 M%, LiAsF_6 ~15 M% and solvent mixture ~70 M%. The PAN-based electrolyte containing EC, PC and LiAsF_6 gave a conductivity of 10^{-3} (S/cm) at room temperature. Both carbon and lithium cobalt oxide composite electrodes were studied versus lithium in small capacity cells. The same electrolyte composition was used in fabricating the composite electrodes. Cells were fabricated and evaluated for cycle life and cathode utilization efficiency. The capacity of the cells is between 5 to 10 mAh. Lithium polymer cells containing either carbon or lithium cobalt oxide showed so far around 40 cycles with minimum 10 s of capacity. Lithium ion polymer cells ($\text{Li}_x\text{C/gel/Li}_x\text{CoO}_2$) delivered ~5 mAh capacity in the initial cycles and cycling of the cell is in progress.

Introduction

Lithium polymeric electrolyte rechargeable cells are being actively developed for several applications including consumer electronics and electric vehicles. Polymer rechargeable cells have several advantages over the liquid electrolyte cells: these include 1) reduced propensity for lithium dendrites, 2) enhanced interfacial stability, 3) flexible shape etc. However, the problems related to dendrites and inactivity are not completely eliminated at the lithium electrodes. The development in liquid-based cells is focused on the

use of lithium-carbon anodes (termed as lithium ion or "recking-chair" configuration) in place of metallic lithium to reduce the dendrites and thus improve the cycle life. Additionally, the replacement of lithium with lithium-carbon may improve the safety of the cells. An extension of this concept, i.e., use of Li-C for Li, to the polymeric electrolyte cells is thus expected to further reduce the problems of dendrites and interfacial instability. At the Jet Propulsion Laboratory as part of an ongoing secondary lithium battery research effort we have initiated preliminary electrochemical studies on the lithium ion polymer cells. Initially, we evaluated the materials properties in small capacity cells. We report below our results on the electrochemical properties of PAN-based gelled electrolytes containing EC + PC + LiAsF_6 as well as on the cycling behavior, at room temperature, of Li-C , Li-LiCoO_2 , and Li_xCoO_2 cells containing the above electrolyte.

Experimental

Electrolyte Preparation:

Gelled electrolytes with different compositions were prepared as given below¹. Appropriate amounts of the components were weighed before hand. Lithium hexafluoroarsenate was dissolved in the solvent mixture and the temperature of the liquid electrolyte was raised to 100°C followed by the slow addition of PAN. The temperature was maintained at around 100°C till a clear homogeneous viscous liquid was obtained. Thin films were prepared by casting the hot gel between two preheated quartz plates and pressing them together. This procedure yielded thin films with thicknesses ~100 micron. Typical composition of the electrolyte was PAN ~15 M%, LiAsF_6 ~15 M% and solvent mixture ~70 M%.

Composite Electrodes Preparation:

Composite electrodes with good ionic and electronic conductivities are required in polymer cells to achieve reasonable rates. Li_xCoO_2 -based composite cathodes were used for cell studies. Composite cathodes comprises of Li_xCoO_2 50 w%, acetylene black (for electronic conductivity) 10 w%, and the polymer electrolyte (for ionic conductivity) 40 w%. The Li_xCoO_2 and acetylene black were well mixed by a high speed blender. Gelled polymeric electrolyte (PAN 15 M%; LiAsF_6 15 M% and EC+PC 70 MO/o) was prepared beforehand followed by the addition of the mixture of Li_xCoO_2 and acetylene black. The hot black slurry was then poured on to a preheated aluminum foil. The slurry was uniformly distributed and coated on the aluminum foil. The composite electrode was cut to size, $1\frac{3}{8}'' \times 1\frac{3}{8}''$, for later use.

The carbon electrode consists of a commercial graphite subjected to a pretreatment process identified in our earlier studies in organic liquid electrolytes. The carbon electrode gave 240 mAh/gm capacity at C/10 rate. The selected carbon anode and electrolyte materials are being used in conjunction with lithium cobaltoxide composite cathode to fabricate Li-ion-polymer cells. The electrodes are sealed in a polyethylene laminated aluminum foil using a sealing technique developed at JPL. Li_xC -based composite electrode was prepared and its electrochemical performance tested. Composite cathodes comprises of Carbon 50 w% and the polymer electrolyte 50 w%. Gelled polymeric electrolyte (PAN 15 M%; LiAsF_6 15 M% and EC+PC 70 MO/o) was prepared beforehand followed by the addition of preweighted carbon. The hot black slurry was then poured into a stainless steel (SS) mold with a 1 mil thick SS. foil on the bottom. The slurry was then evaporated by convection. The composite electrode was trimmed to size, $1\frac{3}{8}'' \times 1\frac{3}{8}''$, for cell studies.

Cell Fabrication:

Three types of cells were fabricated. The three types of cells are 1) $\text{Li/gel/Li}_x\text{CoO}_2$, 2) $\text{Li/gel/Li}_x\text{C}$, and 3) $\text{Li}_x\text{C/gel/Li}_x\text{CoO}_2$. Two polyethylene laminated aluminum foils were hot sealed on three sides to form an envelop. An electrode stack consisting of lithium anode,

polymeric electrolyte, and composite electrodes was assembled and housed in the polyethylene laminate and aluminum envelop. The envelop was sealed in vacuum. Four of each experimental $\text{Li-Li}_x\text{CoO}_2$ and Li-Carbon polymer cells (~ 10 mAh) were prepared for electrochemical investigations. The cells were assembled in a dry-room with less than 1% humidity. Both types of the cells showed an open circuit voltage (WV) in the range of 3.0 and 3.2 volts.

Standard electrochemical equipment were used for the electrochemical evaluation of the gelled electrolyte films. AC impedance measurements were made on both uncycled and cycled cells to obtain informations on the bulk and interfacial properties.

Cell Testing:

The laboratory lithium-composite polymer cells were tested at ambient temperature for cycle life performance between the voltage limits described above. A computer controlled battery cycler was used for cycling studies. The cells were charged at a constant current, 1 mA, and followed by taper charge at 4.25V. The cell was discharged at a constant current, 2 mA. The $\text{Li-Li}_x\text{CoO}_2$ cells were cycled between 4.3V and 2.6V, and the Li-Carbon cells were cycled between 0.15V and 1V. The full cell was cycled between 2.60 V and 4.25 V.

Results and Discussion

We have investigated the electrochemical properties of the gelled polymer electrolytes, three different types of polymer cells and their cycle life performance. These are described below.

Electrolyte Studies:

Electrolyte films were cut to size ($\sim 1\text{cm}^2$) and sandwiched between two well polished stainless steel (SS) electrodes (blocking contacts) for both a-c and d.c measurements. The a-c measurement was made in the frequency regime 100 kHz to 5 Hz. In Fig.1 is shown the Nyquist plot for the electrolyte of composition PAN \sim 15M%, LiAsF_6 \sim 15M% and EC+PC \sim 70 M%. The x-axis intercept gives the bulk resistance (R_b) of the electrolyte. The

resistivity (ρ) is 10^{-3} S/cm at room temperature. The near perpendicular plot indicates that there is no measurable charge transfer at the interface. In Fig. 2 is shown the d-c voltammetric behavior for the same electrolyte. The electrolyte seems stable in the voltage range 1 to 5 V vs. Li.

Electrochemical Studies of Cells:

Although our aim is to evaluate the a-c behavior of the full cells (LiC composite anode/gelled electrolyte/LiCoO₂ composite cathode) as initial studies we investigated the interfacial on bulk properties of the components electrodes using a-c measurements. Experimental cells with Li anode, LiCoO₂ composite cathode (~ 10 mAh) and gelled electrolyte were fabricated and cycled at room temperature. In Fig. 3 is shown a-c behavior of lithium cobalt oxide before and after 39 cycles. The value indicate the total resistance is around 2.1 ohms and did not change with cycling. However, Fig. 3b (a-c behavior of the cycled cell) shows the evolution of a semicircle which indicates that interface (between lithium and electrolyte, electrolyte and cathode, or both) changes continuously. In Fig. 4 is shown the a-c behavior of lithium-lithium carbon cell before and after 33 cycles. Although the bulk resistance of the cell is the same (around 2.1 ohms) the interfacial charge transfer resistance is considerably reduced after cycling. This suggests that probably the interface has improved with cycling.

Cell Performance

In Fig. 5 is shown charge-discharge curves as a function of time up to 42 cycles. for a lithium-lithium cobalt oxide cell. The capacity of the cell declined slowly to 3.7 mAh till ~ 40 cycles. The cycling data for lithium-lithium carbon cell is shown in Fig. 6. The first half cycle is the lithiation of the carbon electrode. A total of 46 mAh was passed. The following cycles exhibited approximately 3 mAh capacity. The capacity difference between the first and the following cycles is attributed to the formation of the surface layer on the carbon material². The discharge capacity for the subsequent cycles remains the same around 3 mAh.

The first three charge-discharge cycles on a full cell (lithiated carbon composite anode/gelled

electrolyte/lithium cobalt oxide composite cathode) is shown in Fig. 7. The cell was cycled between 4.25 V and 2.6 V. The initial capacity of the cell was around 5 mAh. The second and third cycles showed a lower capacity. The cycling of the cells is in progress. The data described above are preliminary and further cell studies are in progress.

Conclusions

PAN-based gelled electrolytes were prepared and electrochemically evaluated. The bulk conductivity at room temperature of the electrolyte PAN 21 M%, LiAsF₆ 8 M% and PC 71 M% was 10^{-3} S/cm. Small capacity experimental half cells with LiC and LiCoO₂ composite electrodes were fabricated and tested for cycle life. These cells could be cycled over 30 cycles without perceptible capacity decline. Performance of the lithium ion polymer cells (LiC/gelled electrolyte/LiCoO₂ cathode) is currently being evaluated and the results will be presented in the meeting.

Acknowledgment

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References

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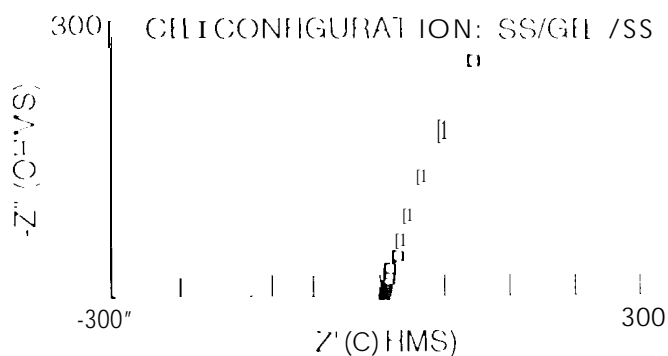


Figure 1. Nyquist plot for the electrolyte containing PAN ~20 w%, LiAsF_6 15 w% and solvent mixture ~65 w%.

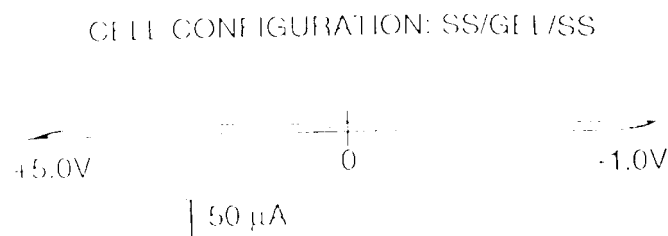


Figure 2. D-C cyclic voltammetric behavior of the electrolyte (same as in Fig. 1) sandwiched between two well polished stainless steel electrodes

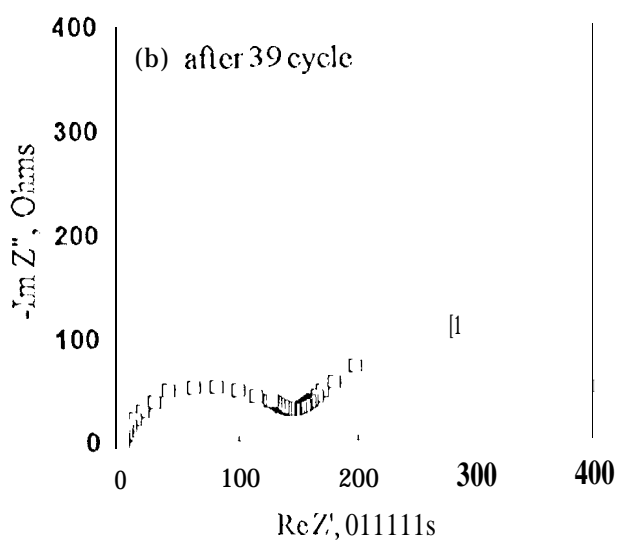
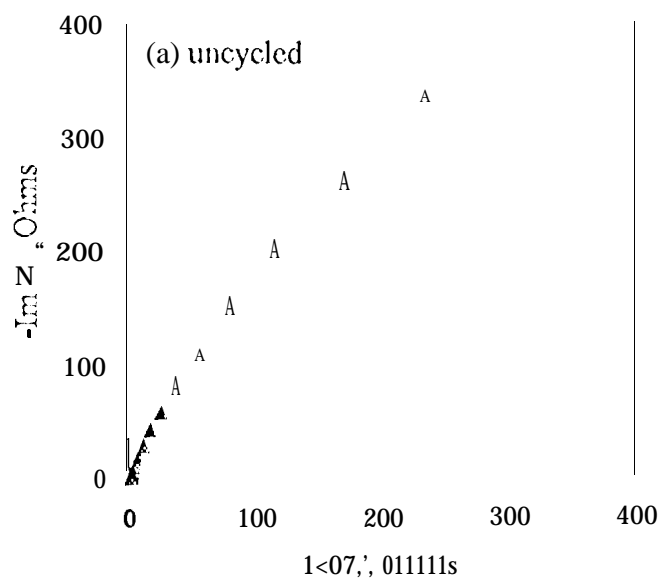


Figure 3. The a-c behavior of lithium-lithium cobalt oxide cell (a) uncycled and (b) after 39 cycles.

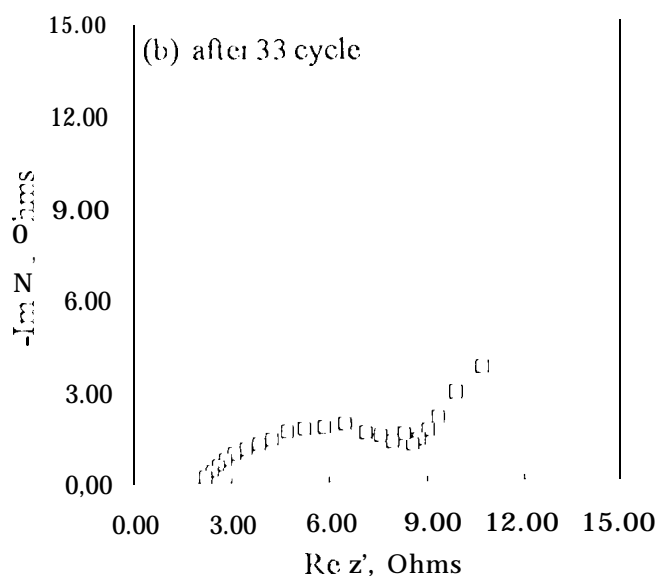
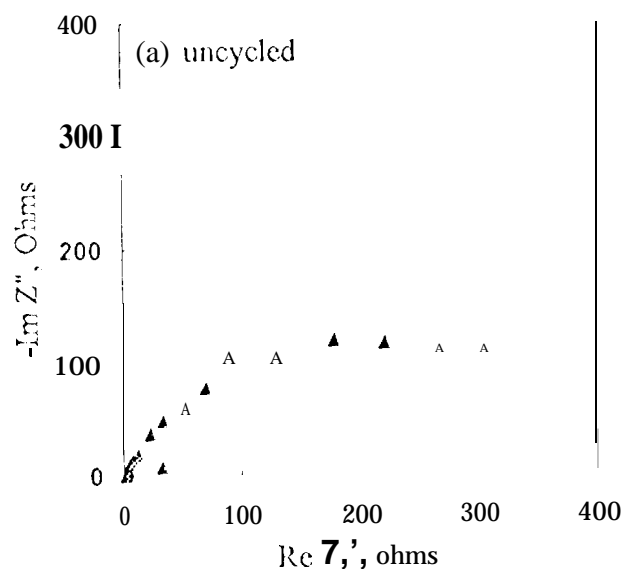


Figure 4. The a-c behavior Of lithium -lithium carbon cell (a) uncycled and (b) after 33 cycles.

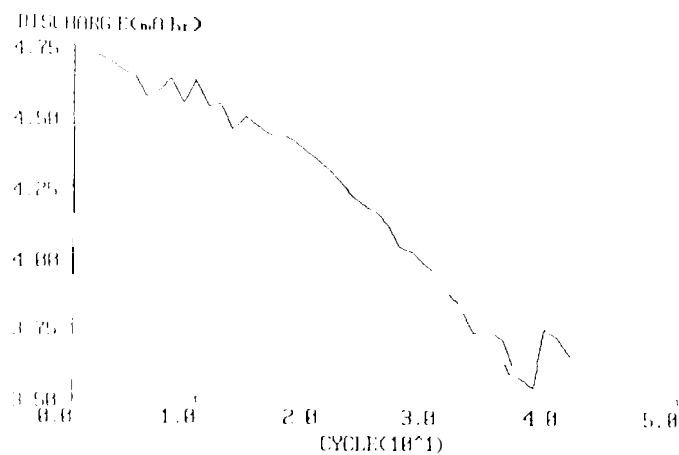


Figure 5. The discharge capacity vs. cycle life of a lithium - lithium cobalt oxide cell.

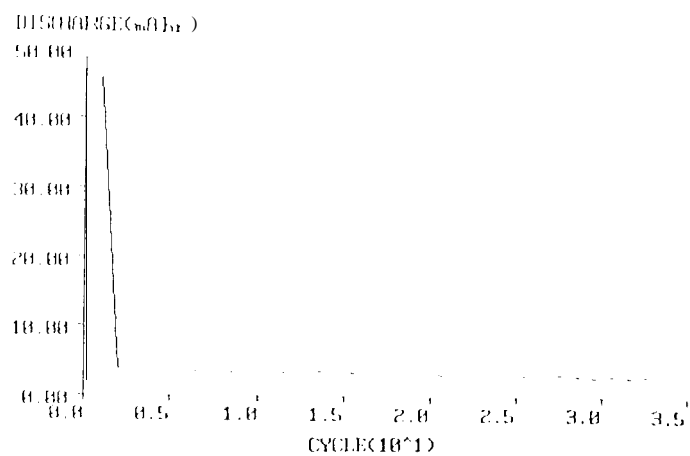


Figure 6. The discharge capacity vs. cycle life of a lithium - lithium carbon cell.

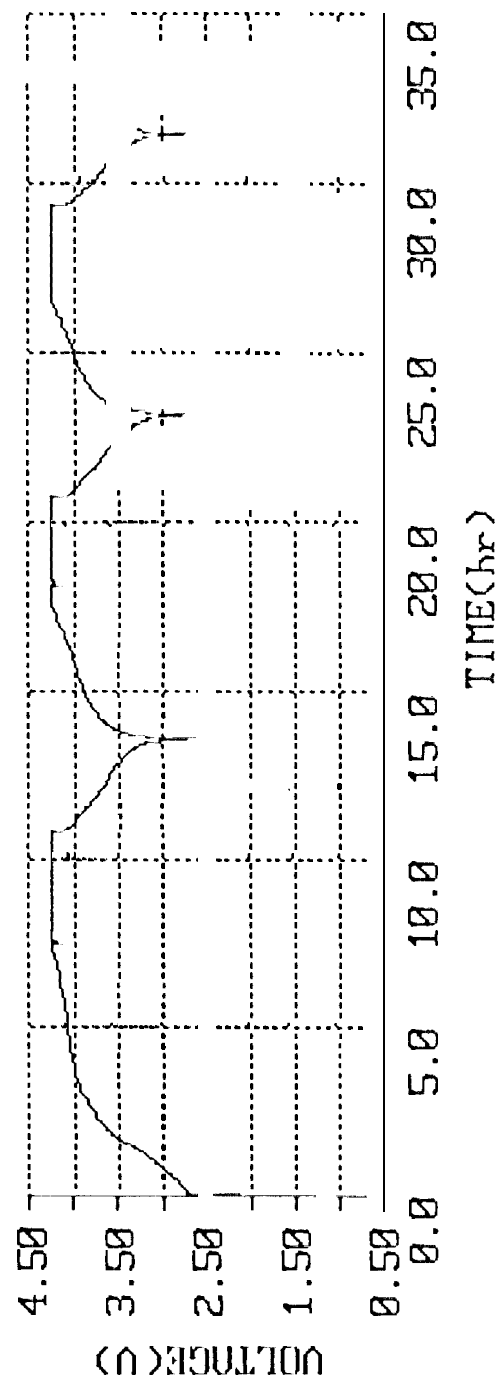


Figure 7. The first three charge-discharge cycles on a full cell (lithiated carbon composite anode/gelled electrolyte/lithium cobalt oxide composite cathode)